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Seasonal changes in chemical and mineralogical composition of sewage sludge incineration residues and their potential for metallic elements and valuable components recovery

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Abstract

The incineration products composition is dependent on the incineration technology, operating conditions and also on the waste feed composition, which can change seasonally, depending on the temporal growth of the population due to tourism, micro-industry seasonality, intensity of atmospheric precipitation and other factors. Seasonal variations in potentially valuable elements concentrations in incineration products are visible but their overall content is low, therefore this material should not be considered as a source of valuable elements. Due to high content of phosphorus (7.5 wt%) only the fly ash can be considered as a potential source of this critical raw material.

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Keywords: sewage sludge; thermal treatment residues; seasonal changes; mineralogical and chemical composition

1. Introduction

Waste thermal treatment (waste incineration) is one of the accepted, by the EU Commission, ways to restrict the excess waste. The EU Member States have committed themselves to reduce significantly the amount of waste produced and landfilled, as well as, to use their energetic and raw materials potential. Waste incineration leads to

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formation of incineration products such as bottom ash, fly ash, air pollution control residues, exhaust gas with suspended dust and wastewater.

Due to the population growth the amount of sewage sludge produced as a result of wastewater treatment increases. That brings the challenges to its proper management. Municipal wastewater is a mixture of household, small industrial plants, trading and service firms sewage and rainfall water [1] and therefore sewage sludge obtained as a result of wastewater processing can be treated as a sink for different contaminants. Due to the fact that sewage sludge can easily accumulate metals, harmful elements and toxic organic substances [2] its landfilling is not recommended [3]. Nevertheless, in developing countries this way of waste treatment is still active. In Poland, landfilling was significantly reduced (74% in 2010 down to 57% in 2014) however still dominating and the higher amount of sewage sludge is thermally treated (increase from 0.4% in 2010 up to 15% in 2014) [4,5]. Even though the sewage sludge thermal treatment has advantages such as volume reduction or lower disposal costs it is not a complete method [6] (still ca. 3% of the solids remain as thermal treatment residues) it aims to minimize the future landfill, or completely avoid it (zero-waste-policy).

As a result of sewage sludge thermal treatment solid residues such as fly ash (FA) and air pollution control (APC) residue are produced. In addition this process leads to volume and mass reduction that causes concentration of elements. The goal of this study was to characterize FA and APC residue from a sewage sludge incineration plant to describe seasonal variation in chemical composition based on main elements (Si, Al, Fe, Ca, P and C_{tot}) and economically valuable trace elements with a focus on: Zn, Pb, Cu, Ni, Cd and Cr as well as to describe mineral composition of incineration residues and the possibility of metallic elements extraction.

2. Material and Methods

2.1. Fluidized bed incineration

Dewatered sewage sludge was incinerated in the fluidized bed boiler using Pyrofluid™ technology, which is characterized by high turbulence of the fluidized bed at operating temperature in the range of 850-900º C, ensuring complete incineration of organic matter, a longer life time of the boiler and the effective reduction of NOx emission. In addition the heat exchange area within the fluid bed allows to reduce the size of the installation. A thermal utilization station is equipped with a heat exchanger, responsible for pre-cool of flue gases and the production of saturated steam to power the drying node. A detail description of incineration technology is presented in [7,8].

2.2. Fly ash (FA) and air pollution control (APC) residue characterization

FA, classified as non-hazardous waste (waste code: 19 01 14) [9], and APC residue (classified as hazardous waste; waste code: 19 01 07*) [9] were sampled quarterly from winter 2015 until autumn 2016, from one of the Polish sewage sludge incineration plants located in a ca. 1 million inhabitants city in Poland. For each sampling 10 kg of averaged FA, and 5 kg of APC were collected from the silo during chutes to the transporting trolleys.

FA was reddish, fine material, which contained over 30% of fine fraction (0.25-0.63 mm particle size) and low content of water soluble fraction, whereas APC was grey, very fine material which contained over 99% of 0.25-0.63 mm fraction, and the content of water soluble fraction exceeded 95% [8]. After removal of the water soluble fraction in the reaction with deionized water (20 L of water was used to filtrate 1000 g of the material) an additional mass reduction of 98% was noted.

2.3. Methods

In order to determine the content of major and trace elements multi-element chemical analysis using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) were performed in the Bureau Veritas Minerals (former AcmeLabs Analytical Laboratories) in Vancouver, Canada. The C_{tot} and S_{tot} content was measured using a LECO combustion analysis and loss on ignition (LOI) was obtained using thermal methods.

The main mineral phases were determined using the Philips X'Pert Diffractometer (APD type) with a PW 3020 vertical goniometer. The range for XRD analyses was 2-64° θ, Cu Kα radiation, a step size of 0.02° and a time of 2 s/step were applied. For phase identification, the Philips X'Pert Graphics and Identify v.1.2a software with the ICDD PDF database was used.

Detailed microscopic observations were performed using the scanning electron microscope (FE-SEM) Hitachi S-4700 equipped with energy dispersive spectrometer (EDS) with Noran Nordlys II detector. These studies enabled determination of the chemical composition of minerals using the spot analyses or micro-area analytical mode. A detailed mineralogy of the studied minerals based on chemical analysis, determination of the relationship between the components, their forms of occurrence within the crystalline and amorphous phases were analyzed. The FA and APC, prepared as thin sections and as scattered powders were carbon coated. Analyses were performed at accelerating voltage 20 kV, using secondary electron (SE) and back scatter electron (BSE) images mode.

3 Results

3.1. Mineral composition of FA and APC residue

The FA was a Si-P-Ca-Fe-Al dominated material. The main minerals detected in XRD analyses in fly ash were quartz (SiO_2), hematite (Fe_2O_3), whitlockite ($Ca_9(Mg,Fe)(PO_4)_6(PO_3OH)$) and feldspar ($K(AlSi_3O_8)$-$Na(AlSi_3O_8)$-$Ca(Al_2Si_2O_8)$). In Fig. 1a-d these minerals are shown respectively, in their most characteristic morphologies observed in FA samples, using the scanning electron microscope.

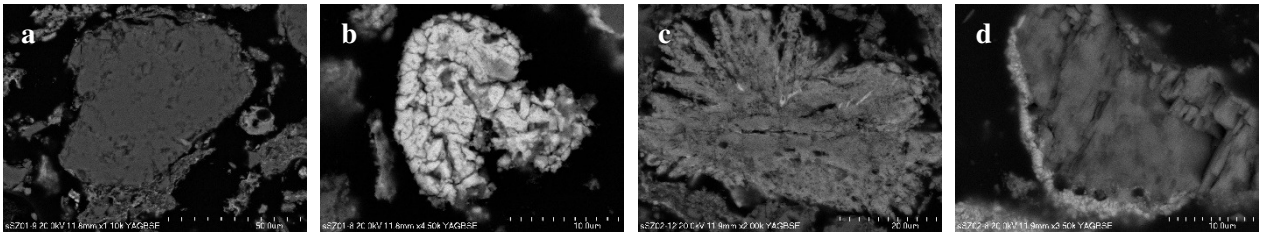

Fig.1 (a) Quartz with rounded edges; (b) hematite microcrystals grouped into a partly rounded assemblage; (c) radial whitlockite; (d) partly rounded K-feldspar surrounded by Fe oxides.

The APC residue composition was dominated by Na-rich the soluble phases. The removal of soluble phase (~98% of the material) from the APC residue by dissolution in deionized water caused significant mass reduction and concentration of non-soluble components. The dominant mineral phases in the APC residue before removal of the water soluble fraction was thenardite ($Na_2(SO_4)$), and in lower amount calcite ($Ca(CO_3)$), apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) and quartz (SiO_2) were present. Different morphologies of thenardite, crystallized from dissolved and dried soluble material from the APC residue are shown in Fig. 2a-d.

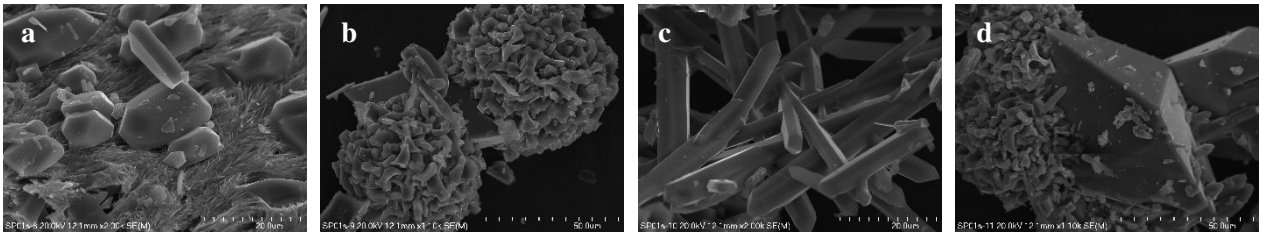

Fig. 2 (a) Fibrous thenardite covered with NaCl crystals; (b) bone-like thenardite grouped in a rounded; (c) thin bar-like thenardite irregularly distributed assemblages; (d) bipyramidal thenardite crystals surrounded by bone-like assemblages.

3.2 Seasonal variation in chemical composition of FA and APC residue

Based on the chemical composition obtained using ICP-MS and ICP-OES methods it was possible to observe seasonal changes in the chemical composition of FA and APC residue during the one year period. The content of main elements such as Si, Al, Fe, Ca and P was rather stable over the year in FA. Only slight variations were observed for Si (relative increase in the summer time; from 16.4 wt% in winter and 16.5 wt% in spring to 18.9 wt% in summer and 18.2 wt% in autumn) and Al, Fe and P (relative decrease in the summer time) and Ca (relative decrease in autumn; Fig. 3a-e). High phosphorus content in FA (av. 7.5 wt% and rather stable) can be referred to the P ore (6-8 wt% P) according to [10], both in the form of phosphate minerals as well as dispersed within minerals can be treated as an important source of this critical raw material.

The variations of the main elements in the APC residue (Fig. 3a-e) show a characteristic pattern, especially visible after removal of soluble minerals, in which concentrations of main elements during the one year period were only slightly changed, except for the summer, where a significant increase in the content of Si, Al, Fe and P was observed. In the case of Ca the concentration was the highest in the cold periods whereas the lowest in the spring, however we expect that this variation could be dependent on the FA and APC residue distribution within the incinerator and not necessarily external factors such as for example atmospheric precipitation.

The C_{tot} variation in a wide range was visible after removal of the water soluble fraction (Fig. 3f). The other main component concentrations (Na, K, Ti, Mg and Mn) were low and remain rather invariable. As suggested by Rachakornkij [11] and Chandler et al. [12] the composition of fly ash is strictly dependent not only on the incineration technology and operating conditions but also on the waste feed composition. The composition of sewage sludge is variable and can fluctuate annually, seasonally but also on a daily basis [12,13]. This is closely related to the rainfall intensity, that causes more intensive flush of mineral and organic pollutants to the sewage wells. Most of the metallic elements are concentrated in FA as the result of elements fractionation during the thermal treatment, what was already observed in sewage sludge incineration residues [7], but also in other types of residues from the thermal treatment of waste [14]. The concentrations of trace elements were relatively stable during the one year period for FA (Fig. 4a-f), except for Cr for which the concentrations dropped down 50% in autumn (526.7 ppm) in comparison to the content in winter (1047 ppm).

In APC (Fig. 4a-f) residue for all selected elements the highest concentrations were measured in winter 2015, then a massive drop was observed in spring, slight increase in summer, and slight decrease in autumn. The same pattern was observed for all elements except for Cr. At this time of interpretation it is difficult to determine if the summer increase in trace element concentrations is an annual trend or a result of one-off touristic/religious event which occurred in that time in the discussed locality (3 million participants). Angelidis and Aloupi [15] reported increased concentrations of Zn, Pb and Cu in household sewage sludge in the summer period due to the population growth caused by high season in tourism. In addition, in summer 2016 in the studied area was characterized by high atmospheric precipitation that could deliver more solid particles containing selected metals (Zn, Pb, Cu, Ni and Cd) washed out from the streets to the storm sewers.

Interestingly, we observed a positive correlation in the content of Zn, Pb, Cu, Ni and Cd that can be interpreted that all of these elements could have one common source, more likely mixed domestic and small industrial plants.

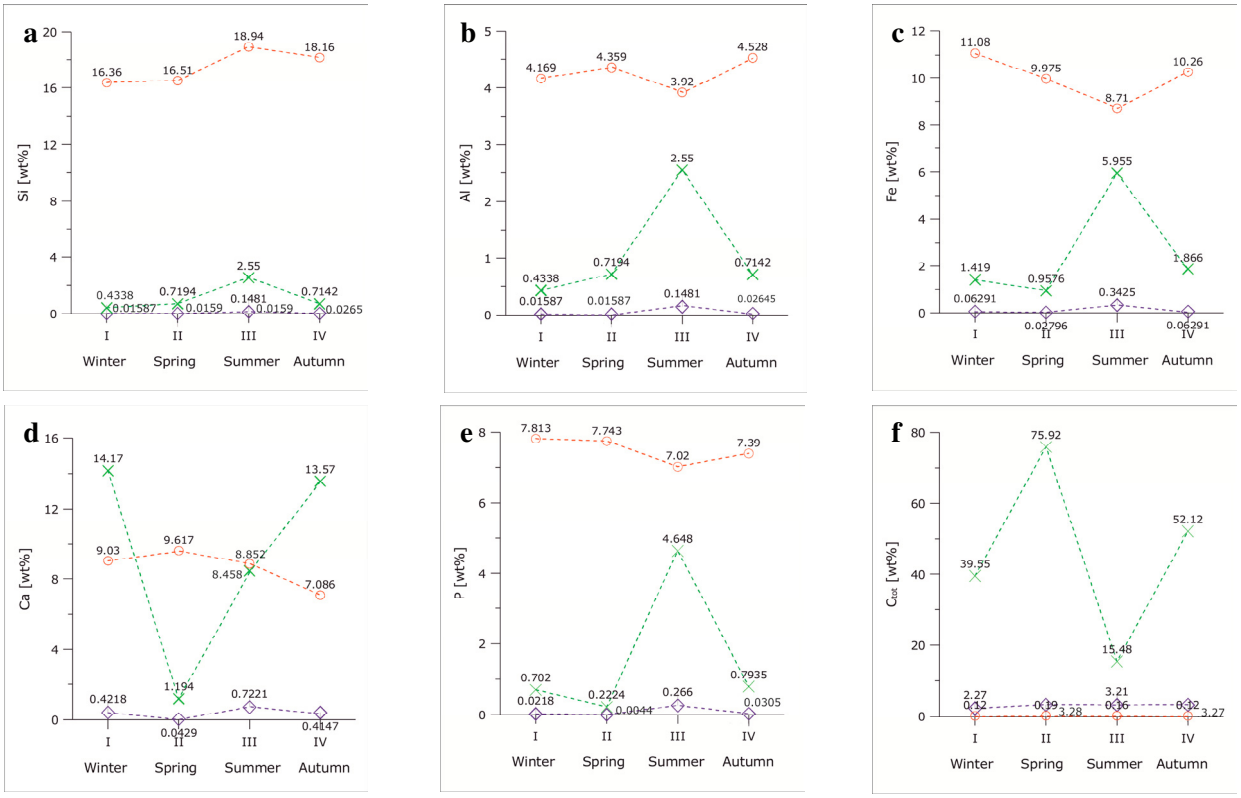

Fig. 3 The concentration of main elements in FA (red dots) and APC (blue diamonds). Green × refers to the composition of APC after removal of soluble minerals (~2-3 wt% of the APC). Dashed lines show extrapolations for (a) Si; (b) Al; (c) Fe; (d) Ca; (e) P and (f) C_{tot}.

As suggested by Ustün [16] domestic source of Zn, Pb and Cu can be tap water, food, detergents, cosmetics. Ni source as suggested by Chandler et al. [12] can be either household or small industrial plants. Cr and Cd can be supplied mostly from small scale industrial plants (food processing, restaurants, medical, dental facilities, garages, car wash, workshops, plastic hardeners etc.). Of course the presence of Cr and Cd in domestic effluents could also be possible. In addition, high concentrations of trace elements in winter time could be attributed to leaching of these elements from metallurgical slags which were applied as an anti-slippery street ballast. As suggested by [17], pet dogs can serve as a carrier for all mentioned heavy metals.

In addition we observe a negative correlation between C_{tot} and metallic elements content in APC, especially visible after soluble material removal. We assumed that metal content could relatively increase as a result of a decomposition of biodegradable organic matter in wastewater treatment plant by microorganisms.

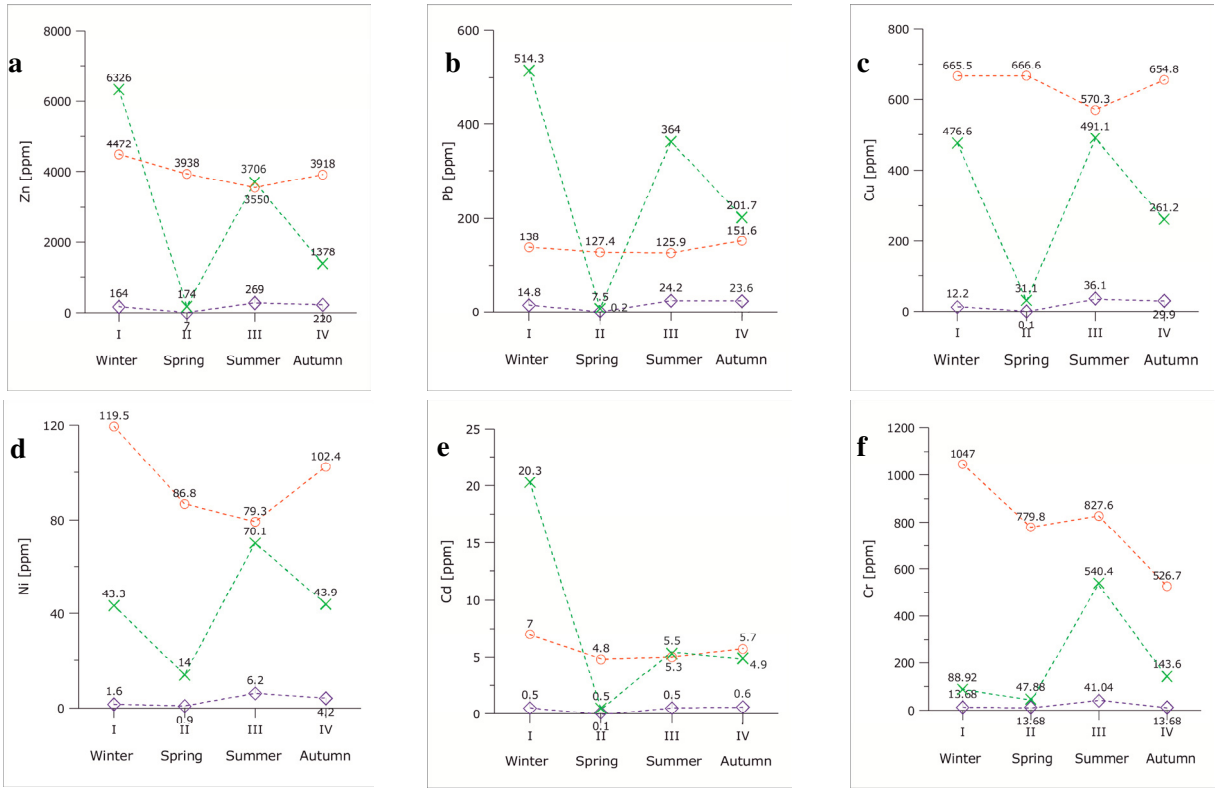

Fig. 4 The concentration of trace elements in FA (red dots) and APC (blue diamonds). Green × refers to the composition of APC after removal of soluble minerals (~2-3 wt% of the APC). Dash lines show extrapolations for (a) Zn; (b) Pb; (c) Cu; (d) Ni; (e) Cd and (f) Cr.

4. Conclusions

Even though the seasonal variations in metallic and/or potentially valuable element concentrations are visible their overall content is low. In addition, they do not create their own minerals but are dispersed within crystalline and amorphous phases, therefore it seems to be inappropriate to consider this material as a source of valuable elements without elaboration and application of cheap and effective extraction techniques. Due to the high content of phosphorus (7.5 wt%) only FA can be considered as a potential source of this critical raw material**.**

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